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(21) International Application Number: PCT/US00/03490 (22) International Filing Date: 08 February 2000 (08.02.2000) (30) Priority Data: 09/247,363 10 February 1999 (10.02.1999) US (60) Parent Application or Grant KING INDUSTRIES, INC. [/]; O. HE, Zhiqiang, Alex [/]; O. BLANK, Werner, J. [/]; O. PICCI, Marie, E. [/]; O. LIN, Maria, C., H. ; O.		Published
(54) Title: BISMUTH CARBOXYLATES AS CATALYSTS FOR CROSSLINKED BLOCKED ISOCYANATE WATERBONE COATINGS (54) Titre: BISMUTH CARBOXYLATES UTILISES COMME CATALYSEURS POUR REVETEMENTS RETICULES A BASE AQUEUSE D'ISOCYANATE BLOQUE (57) Abstract <p>A catalyst for the crosslinking of a cationic resin with a blocked isocyanate having low environmental toxicity and with activity in waterborne coatings comprises a salt of bismuth and a carboxylic acid with a hydrocarbon chain of from 11 to 36 carbon atoms and a molecular weight of from 165-465.</p> (57) Abrégé <p>Cette invention concerne un catalyseur destiné à la réticulation d'une résine cationique avec un isocyanate bloqué qui présente une faible toxicité pour l'environnement et une activité dans les revêtements à base aqueuse. Ce catalyseur comprend un sel de bismuth et un acide carboxylique avec une chaîne hydrocarbonée de 11 à 36 atomes de carbone et un poids moléculaire compris entre 165 et 465.</p>		

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(21) International Application Number: PCT/US00/03490 (22) International Filing Date: 8 February 2000 (08.02.00) (30) Priority Data: 09/247,363 10 February 1999 (10.02.99) US (71) Applicant: KING INDUSTRIES, INC. [US/US]; Science Road, P.O. Box 588, Norwalk, CT 06842 (US). (72) Inventors: HE, Zhiqiang, Alex; 58 Silver Spring Road, Ridgefield, CT 06877 (US). BLANK, Werner, J.; 89 Spectacle, Wilton, CT 06897 (US). PICCI, Marie, E.; 146 New Canaan Avenue, Norwalk, CT 06850 (US). (74) Agent: LIN, Maria, C., H.; Morgan & Finnegan, L.L.P., 345 Park Avenue, New York, NY 10154 (US).			(81) Designated States: CA, JP, KP, KR, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: BISMUTH CARBOXYLATES AS CATALYSTS FOR CROSSLINKED BLOCKED ISOCYANATE WATERBONE COAT- INGS (57) Abstract A catalyst for the crosslinking of a cationic resin with a blocked isocyanate having low environmental toxicity and with activity in waterborne coatings comprises a salt of bismuth and a carboxylic acid with a hydrocarbon chain of from 11 to 36 carbon atoms ana a molecular weight of from 165-465.			

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Description

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Bismuth Carboxylates as Catalysts for Crosslinked Blocked
Isocyanate Waterborne Coatings

INTRODUCTION

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The present invention is directed to a method of catalyzing the process for de-blocking blocked isocyanates to form crosslinked coatings. More particularly, the present invention relates to the use of certain bismuth carboxylates that are effective in catalyzing both a solvent borne and a waterborne process to form such crosslinked coatings.

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The bismuth carboxylates of the present invention are useful at a very low concentration of 0.05-0.5 wt% of metal based on the total resin weight and are highly effective. This is very desirable in that the emission into the environment of bismuth, a low toxicity metal, is reduced to very low levels.

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BACKGROUND OF THE INVENTION

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Blocked isocyanates have been used in many coating applications, such as powder coatings, electrocoatings, coil coatings, wire coatings, automotive clear topcoatings, stone chip resistant primers, and textile finishes. Traditionally, these coating processes employ organic solvents, which may be toxic and/or obnoxious and cause air pollution. In recent years, the legal requirements for low or no pollution of the environment have led to an increase in the interest in waterborne and high solids coatings.

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In processes wherein blocked isocyanates are used, heating to an elevated temperature is necessary to remove the blocking group from the blocked isocyanate to form free isocyanates. The free isocyanates then react with polyols (polymers containing hydroxy functional groups) to form a crosslinked network as a thin film coating. An obstacle to the use of this process is the high temperature required to remove

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5 the blocking group. The process is extremely slow without a
catalyst. It is known that metal compounds such dialkyltin and
certain bismuth and zinc salts are excellent catalysts in these
10 solvent borne coating processes. "Crosslinking with
5 Polyurethanes." W.J.Blank, ACS Proceedings of Polymeric
Materials Science and Engineering (1990) 63:931-935.

15 Bismuth organo-compounds have been used in a variety
of processes wherein polyisocyanates or blocked isocyanates is
an ingredient. For example, EP 95-109602 describes an epoxide
20 amine adduct with a bismuth compound as being useful in a
conventional cationic coating process. US 5,702,581 describes
25 the use of organic bismuth complexes in phosphate dip coating
compositions to provide corrosion resistance. The bismuth
organic complexes include bismuth carboxylates, such as bismuth
lactate. WO 95/29007 disclosed the use of bismuth
30 compounds/mercapto complexes for curing polyisocyanate organic
solvent compositions. The bismuth compounds disclosed include
bismuth carboxylates, nitrates and halides. WO 96/20967 also
described bismuth/zinc mixture with a mercapto complex as a
35 catalyst for producing polyurethane. See also Frisch et al.,
"Novel Delayed-Action Catalyst/Co-catalyst system for C.A.S.E.
Applications", 60 Years Polyurethanes, Kresta et al. ed.,
Technomic: Lancaster, PA 1998, pp. 287-303. Further, WO
95/08579 described bismuth/mercapto complexes as latent
40 catalysts in a polyol-polyisocyanate adhesive system. The
catalyst is described as useful in promoting the rapid cure of
the system. The bismuth carboxylates described in these
references are those wherein the carboxylate has ten carbons or
less in the hydrocarbon structure. These conventional bismuth
45 carboxylates do not provide improved resin performance nor are
they effective in water-borne formulations.

50 WO 95/07377 described the use of bismuth lactate in
cationic lacquer compositions, which employ urethane reactions.

5 A mixture of bismuth and an amino acid or amino acid precursor
was disclosed for catalyzing a cationic electrodeposition of a
resin film on a metal substrate. The bismuth may be present in
10 the form of nitrates, oxides, trioxides, or hydroxide. DE
5 19,532,294A1 also disclosed bismuth carboxylates as catalysts
for single component polyurethane lacquer coatings in a solvent
borne formulation.

15 Unfortunately, when the known bismuth catalysts are
employed in waterborne coatings formulations, it was found that
10 they were not effective. It is suspected that the loss of
activity is related to the hydrolysis of the bismuth salt in
20 water. Moreover, even if these compounds function as catalysts
in waterborne processes, it has been our experience that a very
high level is necessary, usually 10 to 100 times higher than in
25 solvent borne processes. This is undesirable because bismuth
has a low degree of toxicity and would cause environmental
pollution if a large amount is released into the environment.

30 Bismuth carboxylates have been used as catalysts in
processes that do not involve de-blocking of blocked
20 isocyanates. Bismuth dimethylol propionate has been disclosed
in DE 93-43,300,002 as being useful in an electrocoating process
35 for coating phosphate dipped metals to provide anti-corrosion
and weather resistance. Bismuth carboxylates are also described
in DE 96-19,618,825 for use in an adhesive gel formulation that
25 is safe for contact with human skin. The formulation contains
40 polyether polyols with hydroxy groups, antioxidants,
Bismuth(III) C₂-C₁₈ carboxylates soluble in the polyether polyols
and OCN(CH₂)₆NCO. JP 95-351,412 describes the use of bismuth
45 neodecanoate as a catalyst for two part adhesive formulations
30 containing polyisocyanates, polyols with an ethylenediamine.
These formulations do not involve the de-blocking of blocked
isocyanates.

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For waterborne processes, the catalysts known to be useful are organo-tin and lead compounds. See WO 95/04093, which describes the use of organo-tin alone or in a mixture with other compounds including bismuth oxide in a low temperature curing process employing blocked isocyanates. There is no disclosure of bismuth carboxylates alone as a catalyst for de-blocking isocyanates. Organo-tin compounds have also been used in coatings, e.g. in paints for anti-fouling applications. Organo-tin compounds in mixtures with bismuth hydroxy carboxylic acid salt was described in DE19,613,685. The use of bismuth lower carboxylates was described as being useful in a phosphate dip process to provide corrosion resistance to lacquer coatings. The bismuth carboxylates described therein as being useful are lower carboxylate of bismuth wherein the carboxylic acid has up to ten carbons. The substrate is then coated with an epoxy resin in the presence of a blocked isocyanate as the crosslinking agent using a zinc organo compound and/or lead compound as the catalyst. EP0,509,437 disclosed a mixture of a dibutyltin aromatic carboxylate with a bismuth and a zirconium compound as the dissociation catalyst for electrocoating wherein a blocked isocyanate is used. Polystannoxane catalysts are also described in EP0,810,245 A1 as an low temperature catalyst for curing compositions comprising a blocked isocyanate. Bismuth compounds, including carboxylates were described as being useful as a co-catalyst. However, the process is one in which the reaction temperature was in the range of 100°C, quite a bit below the normal temperature of 120°C to 150°C for de-blocking blocked polyisocyanates. JP 94-194950 described a formulation for coating materials which are rapidly curable in contact with an amine catalyst vapor or mist. The coating formulation included polyols, polyisocyanates, antimony or bismuth catalysts with mercaptans in an organic solvent. The toxicity of both lead and tin compounds present serious environmental hazards

5 The use of solvents in solvent borne processes further result in
the undesirable release of toxic and obnoxious chemicals into
the environment. For these reasons, the use of organo tin and
10 lead compounds and solvents has been banned in many applications
5 and is highly restricted in electrocoating.

It is, therefore, important to develop other catalysts
or catalysts systems for waterborne processes.

15 SUMMARY OF THE INVENTION

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Certain bismuth carboxylates have now been developed
20 as effective catalysts for coatings processes wherein a
temperature of at least 130°C is used to de-block blocked
isocyanate employed as the crosslinking agent. The bismuth
15 carboxylates of the present invention are compounds wherein the
25 carboxylate is derived from a carboxylic acid with more than ten
carbon atoms. The bismuth carboxylates of the present invention
have been found to be highly effective and efficient catalysts
and are useful at very low concentrations both in solvent and
30 water-borne processes. Thus, even though bismuth has a low
20 toxicity, the low concentrations required reduces the emission
of bismuth into the environment and thus reduces environmental
35 contamination.

An objective of the present invention is to develop
25 catalysts, which are effective, and efficient for de-blocking
blocked isocyanate to form crosslinked coatings with reduced
40 environmental contamination.

It is a second objective of the present invention to
develop catalysts, which may be used at very low concentration
30 levels to reduce the emission of toxic substances into the
45 environment.

It is a further objective to develop a catalyst, which
is highly effective not only in solvent borne processes, but

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5 retains its high effectiveness in waterborne coating compositions.

10 It is another objective to reduce the emission of metals into the environment.

5 In accordance with the present invention a process has been developed for forming blocked isocyanate crosslinked coatings formulations comprising as a catalyst, a bismuth carboxylate, wherein the carboxylate is derived from a carboxylic acid with a linear or branched hydrocarbon chain of 11-36 carbons. The hydrocarbon chain may contain heteroatoms such as nitrogen, oxygen or sulfur. The carboxylic acid may be aromatic or aliphatic, such as: undecanoic, dodecanenoic, palmitic, stearic, oleic, isostearic, abietic acids. The carboxylic acid may be synthesized or derived from natural fats. 15 The catalyst may also comprise a mixture of the carboxylic acids useful in the present invention.

DETAILED DESCRIPTION OF THE INVENTION

30 20 In accordance with the present invention a catalyst for crosslinked blocked isocyanate coatings has been developed. The catalyst comprise a bismuth salt of a hydrophobic carboxylic acid having 11-36 carbon atoms in the hydrocarbon chain and a molecular weight in the range of 165-465. Preferably the 35 carboxylic acid suitable for the present invention is water-insoluble.

40 The carboxylic acid salts of bismuth of the present invention is prepared by heating 1M of bismuth trioxide, Bi_2O_3 , with at least 3M of a carboxylic acid or an anhydride and 45 30 removing the water from the reaction mixture. The reaction is carried out at a temperature of 120-150°C for several hours or until a clear solution is obtained.. The bismuth carboxylates of the present invention are known to be unstable in the presence 50 of water. They are hydrolyzed and break down into their

5 constituent parts: bismuth oxide and the carboxylic acid from
which they are formed. However, surprisingly, on heating to
130°C, the bismuth carboxylate reforms and is highly effective
10 as a catalyst.

5 This catalyst is also effective in solvent borne
coatings, which contain low levels of water, such as in
pigmented coatings. Furthermore, the bismuth carboxylates of
15 the present invention are stable and have a longer shelf life.

The catalytic activity of the bismuth catalysts useful
10 in the present invention can be maintained if the salt is
prepared from a hydrophobic, carboxylic acid having 11-36
20 carbons in the hydrocarbon chain. The hydrocarbon chain may
comprise non-carbon atoms, such as nitrogen, oxygen or sulfur.
The carboxylic acid may be aromatic or aliphatic with a
25 15 molecular weight in the range of 165-465. The carboxylic acids
useful in the present invention are water-insoluble. In a
water-borne electrocoating process, the cationic resin co-
30 deposit with the hydrolyzed bismuth carboxylate of the present
invention as a mixture of bismuth oxide and carboxylic acid.
20 When heated to a curing temperature of 130°C or above, the
bismuth carboxylate forms in situ to catalyze the process.

35 The carboxylic acid salts of bismuth may be prepared
by heating one mole of bismuth trioxide (Bi_2O_3) with at least 3
moles of a carboxylic acid or an anhydride and removing the
25 40 water formed. The reaction is carried out at a temperature of
120-150°C for 1 to 5 hours or until a clear solution is
obtained. The bismuth carboxylate catalysts of the present
invention are effective in both solvent borne and water borne
45 coatings. It is particularly useful in pigmented coatings.

30 The bismuth carboxylates of the invention may be used
singly or in combination as mixtures. To form a mixture of the
carboxylates, a mixture of carboxylic acids or anhydrides may be
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5 used in the process. The carboxylates may also be prepared in
situ, i.e. a mixture of a bismuth salt such as bismuth oxide or
chloride with carboxylic acid, singly or in mixtures may also be
10 incorporated into the coating formulation.

5 Cationic water-borne resins or cationic electrocoating
resins useful in this invention can be typically prepared by
reacting a bisphenol A type epoxy resin with an epoxy equivalent
15 weight of between 200 to 2000, preferably between 400 to 1000
with an amine. The amine can be ammonia, a secondary, primary
10 or a tertiary amine. If ammonia is used in the preparation of
the cationic resin, the reaction of the epoxy resin with ammonia
20 has to be conducted in the presence of large excess of free
ammonia to suppress gelation of the resin. In this reaction a
combination of primary, secondary and tertiary amine functional
25 15 resin is formed. With primary amines, depending on the ratio of
amine to epoxy secondary, and tertiary amine functional resins
are formed. With secondary amines tertiary amine functional
resins are produced. If an excess of epoxy is used and if the
30 reaction is conducted in the presence of some water and
20 neutralizing acid, there is also the potential for the formation
of quaternary ammonium group containing resins.

35 Another way to prepare cationic resins is by co-
polymerization of cationic monomers such as dimethyl-amino-
propyl-methacrylate, dimethyl-amino-ethyl-methacrylate,
25 20 dimethyl-amino-propyl-acrylamide or t-butyl-amino-ethyl-acrylate
40 with an acrylic or methacrylic ester monomer or optionally with
styrene or acrylonitrile. Other methods are the reaction of
anhydride functional polymers with amines with primary or
secondary and t-amine groups and a mono epoxide compound as
45 30 shown in US 3,984,382.

If a waterborne formulation is desired, an alcohol or
a polyol can be solubilized or dispersed in water in the

5 presence of nonionic groups or a nonionic surfactant. The
alcohol or polyol may be incorporated in the bisphenol epoxy
resin itself. For example, a bisphenol epoxy resin can be
10 reacted with a methoxy-polyethylene glycol or a methoxy-
5 polyethylene-ether-amine with a MW of between 500 to 2000.

Waterborne resin formulations suitable for this
invention may also include resins dispersed in water in the
15 presence of a nonionic surfactant. An epoxy or an acrylic or
polyester resin may be dispersed in water. The nonionic groups
20 can be a part of the resin structure or a part of an external
surfactant. Commercial products, which are suitable, include a
dispersion in water of solid bisphenol A glycidyl resins with a
molecular weight of between 900 to 4000.

The blocked isocyanate crosslinker useful in this
25 invention are aromatic or aliphatic isocyanates with a blocking
group, which can be removed. Often the de-blocking to the
isocyanate is a displacement reaction, wherein the blocking
30 group is displaced with another group. Typical blocking groups
for the isocyanate are selected from the group consisting of
20 malonates, triazoles, ϵ -caprolactam, phenols, ketoxime,
pyrazoles, alcohols, glycols, glycol ethers and uretdiones.

Some typical di or polyisocyanates suitable for the
invention are: hexamethylene diisocyanate, isocyanurate trimer,
biuret, isophorone diisocyanate, tetramethylxylidine
25 diisocyanate and methylene bis(phenyl isocyanate). Typical
examples of blocking groups are methyl ethyl ketoxime, ϵ -
40 caprolactam, 1,2,4-triazole, 3,5-dimethylpyrazole, phenol, 1,2-
ethylene glycol, 1,2-propylene glycol, 2-ethylhexanol, 2-
butoxyethanol, 2-methoxy (2-ethoxy ethanol).
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30 The cationic resins suitable for the invention may
also be typically dispersed in water in the presence of a
suitable water soluble organic acid such as formic, acetic,
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glycolic or lactic acid or an inorganic acid such as sulfamic acid.

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A coating formulation is normally prepared by blending and dispersing the blocked isocyanate crosslinker, the cationic resin and the catalyst of this invention in water. If pigments are added they can be dispersed separately in the resin. If neutralization of the cationic resin with an organic acid is required, the acid can be added to the resin or to the water phase. Usually high shear dispersers are used to emulsify or

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The catalyst of this invention is also advantageous for use in solvent borne coating formulations. Most pigmented formulation have shown a decrease of catalytic activity on aging. This reduction in catalyst activity is attributable to the presence of water on the surface of the pigment. Based on experience, it is known that catalyst deactivation takes place if the coating formulations are cured at high humidity.

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Although the catalyst of the present invention is predominately suitable for waterborne or water-dispersed coatings. It would be advantageous to use a catalyst with a long shelf life in solvent borne coatings, such as a catalyst of the present invention .

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The present invention further includes a coating formulation comprising of polyol, a blocked isocyanate crosslinker and a bismuth carboxylate catalyst. The coating formulation can contain varying amounts of water, depending on the desired application. The bismuth carboxylates of the present invention is a salt of bismuth and a carboxylic acid with a total of between 11 to 36 carbons or a mixture of bismuth oxide or chloride with a carboxylic acid with a total of between 11 to 36 carbons. The carboxylates of the present invention are soluble in a water-immiscible solvent.

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5 The present invention is further directed to a
cationic electrocoating formulation comprising a water-
dispersible cationic polyol, a blocked isocyanate and a bismuth
10 catalyst of the present invention.

5 The water-dispersible cationic polyol is at least di-
functional, preferably tri functional or higher. The blocked
isocyanate is present at a molar ratio sufficient to facilitate
15 crosslinking. The bismuth catalyst is used at a concentration
of between 0.01 to 0.5 weight percent (wt%), preferably between
10 0.1 to 1.0 wt%, of metal based on the total resin solids in the
formulation.

20 The catalyst may also comprise a bismuth salt, such as
an oxide or chloride and not a carboxylate, in combination with
a free carboxylic acid to form the bismuth carboxylate of the
25 present invention in situ. The bismuth carboxylate may be made
from a single or a mixture of carboxylic acids.

Typical carboxylic acids suitable for the present
invention are selected from the group consisting of linear and
30 branched, saturated and unsaturated, aromatic and cycloaliphatic
C₁₁ to C₃₆ mono and di carboxylic acids. Examples of suitable
20 carboxylic acids include undecanoic, dodecanenoic, palmitic,
stearic, oleic, isostearic, abetic acid, etc. These acids can
35 be derived from natural fats or produced synthetically.

The present invention further include coating
25 compositions comprising a polyol, a blocked isocyanate and a
bismuth salt of a water insoluble aliphatic, cycloaliphatic or
40 aromatic, carboxylic acid with a total number of carbons in the
hydrocarbon chain of between 11 to 36. Optionally, the chain
may contain heteroatoms such as oxygen, nitrogen or sulfur. The
45 catalyst of the present invention also includes blends of
30 bismuth salts, such as bismuth oxides and chlorides with the

5 above acids, or a mixture of the bismuth carboxylates as defined above.

10 The bismuth carboxylate of the present invention is added to the resin blend at a concentration of between 0.01 to 5 1.0 wt%, preferably between 0.05 to 0.5 wt%, of bismuth metal based on the total resin weight in the formulation. Preferably the resin is in a waterborne cationic electrocoating formulation 15 system.

10 The following examples are provided to illustrate the present invention and are not meant to limit the scope thereof.

20 Example 1

15 Preparation of a Cationic Bisphenol A Glycidyl resin

25 A cationic resin was prepared by reacting a diglycidylether bisphenol A resin with a secondary amine in accordance with the following formulation.

	<u>Weight</u>	<u>Equivalent weight</u>	<u>M</u>	<u>Ratio</u>
Bisphenol A epoxy	117.3	540	0.217	1
Diethanolamine	22.8	105	0.217	1
2-butoxyethanol	29.4			

40 A commercially available bisphenol A-epichlorohydrin epoxy resin with an epoxy equivalent weight of 540 were dissolved in 2-butoxyethanol and blended with the diethanolamine (1 equivalent of amine). The reaction mixture was heated to 80°C for 3 hours and then held over night. The mixture is 45 adjusted with 2-butoxyethanol to approximately 83 wt% solids. 25 This is a cationic resin, which can be dispersed in water.

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Example 2Blocked Isocyanate Crosslinker

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5 A polymeric aromatic methylene phenyl isocyanate with an average functionality of 2.5 was reacted with an equivalent amount of 2-methoxy(2-ethoxyethanol) until FT-IR showed a complete disappearance of the NCO groups.

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	<u>Weight</u>	<u>Equivalent weight</u>	<u>M</u>	<u>Ratio</u>
20 MDI, polymeric	42.4	131	0.324	1.0
2-methoxy(2-ethoxyethanol)	39.6	120	0.33	1.02

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Example 3Preparation of the coating

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169 parts by weight of the cationic resin of example 1 was blended with 82 parts by weight of the crosslinker of Example 2 and 14.1 parts by weight of a 85 wt% solution of lactic acid in water. A catalyst selected from the following table and added to the mixture in an amount as indicated in the table. 352 parts by weight of de-ionized water was added under high speed agitation to the blend. The blend was permitted to age for 24 hours prior to application. Films were cast on pretreated steel panels at a dry film thickness of 15 micron and baked for 20 minutes at 180°C.

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<u>Catalysts</u>	<u>Metal wt% on total resin</u>	<u>MEK double rubs</u>
No catalyst	0.0	<10
Dibutyltin dilaurate	0.25	10
Dibutyltin dilaurate	0.50	10

5		14	
	Bismuth tris (2-ethylhexanoate)	0.25	100
10	Bismuth tris (2-ethylhexanoate) + 3 M isostearic acid *	0.25	200 200 (after 48 hours)
	Bismuth tris (2-ethylhexanoate) + 1.5 M dimeric fatty acid *	0.25	200 (after 48 hours)

15 * corresponds to 3 equivalent of COOH per Bi and the dimeric fatty acid is a C₁₆ dimeric acid derived from tall oil.

20 The test results on the coating formed from this formulation clearly illustrates the superior performance of a
5 bismuth carboxylate catalyst in the presence of a non-volatile acid during the baking process.

25 Example 4

10 A cationic resin was prepared from a diglycidyl ether of bisphenol A in accordance with the following formulation.

30		<u>Weight</u>	<u>Equivalent weight</u>	<u>M</u>	<u>Ratio</u>
	Bisphenol A epoxy	166.3	875	0.19005	1
35	Diethanolamine	18	105	0.17142	0.9
	2-butoxyethanol	67			

40 A commercially available bisphenol A-epichlorohydrin epoxy resin with an epoxy equivalent weight of 875 is dissolved in 2-butoxyethanol and blended with the diethanolamine (0.90
15 equivalent of amine). The reaction mixture is heated to 80°C for 3 hours and then held over night. The mixture is adjusted with
45 2-butoxyethanol to approximately 73 wt% solids.

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Example 5

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A blocked isocyanate crosslinking agent was prepared in accordance with the formula in the following table. MDI polyisocyanate was reacted with 2-butoxy(2-ethoxyethanol) at 100°C for 4 hours.

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	<u>Weight</u>	<u>Equivalent weight</u>	<u>M</u>	<u>Ratio</u>
MDI, polymeric	51.8	131	0.395	1
2-butoxy(2-ethoxyethanol)	66.6	162	0.411	1.04

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Example 6

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Coating Formulation

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251 part by weight of the cationic resin of example 4 was blended with 118 parts by weight of the crosslinker of example 5 and with 11.5 parts by weight of a 85 wt% solution of lactic acid in water. 618 parts by weight of de-ionized water was added under high speed agitation to this blend. The formulation was aged for 24 hours before application. Films were cast on pretreated steel panels at a dry film thickness of 15 micron and backed for 20 minutes. All catalyzed formulations were formulated with the corresponding catalyst at a concentration of 0.25 wt% metal based on the total resin blend. The catalyst was added to the formulation prior to the addition of water. The coating was applied on phosphate pretreated steel, 15 μ film thickness.

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Solvent resistance Methylethylketone double rubs

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<u>Catalyst\Cure Temp., 20 min.</u>	<u>180°C</u>	<u>170°C</u>	<u>165°C</u>
None	10	10	10
Dibutyltin dilaurate	63	30	10

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Bismuth tris(2-ethyl-hexanoate)	150	70	20
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Bismuth tris(2-ethyl-hexanoate) and 3M of isostearic acid	200	150	20
---	-----	-----	----

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Bismuth tris(2-ethylhexanoate) + 1.5M of oleoyl sarcosine	200	150	70
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This formulation illustrates the substantial improvement in cure response over dibutyltin dilaurate and bismuth 2-ethylhexanoate with 8 carbons. It also illustrates that not only simple carboxylic acids but also a complex acid such as a sarcosine may be combined with bismuth to provide improved cure performance.

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Example 7

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2-butoxyethanol blocked isocyanate

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A polymeric MDI isocyanate is blocked with 2-butoxyethanol. No catalyst was used in the following reaction.

35

	<u>Weight</u>	<u>Equivalent weight</u>	<u>M</u>	<u>Ratio</u>
MDI polymeric	55.0	131	0.395	1
2-butoxyethanol	70.7	162	0.411	1.04

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The polymeric MDI was mixed with the 2-butoxyethanol and held at 100°C for 4 hours.

Example 8

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Coating Formulation

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322 parts by weight of the cationic epoxy resin of Example 4 was blended with 125 parts by weight of the 2-

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5 butoxyethanol blocked MDI crosslinker of Example 7. 12.9 parts
by weight of lactic acid and 589 parts of de-ionized water were
added to this blend. The catalyst was added before the addition
10 of water. The formulations with catalyst contained a catalyst
5 level, which corresponded to 0.25 wt% metal based on the total
amount of binder (resin and crosslinker). The water was added
under high speed agitation.

15 The coating formulations were cast on iron phosphate
pretreated steel and cured for 20 minutes at the indicated
10 temperature. The dry film thickness was 30 micron. Solvent
resistance was measured as methyl ethyl ketone double rubs.

25	<u>Aging Period</u>	<u>24 hrs</u>	<u>1 week</u>	5 days, 0.6 mils <u>thickness</u>	<u>5 days</u>
	Cure temp, °C	180	180	180	170
	No catalyst	10	10	10	10
30	DBTDL	200	80	50	50
	Bismuth tris(2-ethylhexanoate)	200	200	100	50
35	Bismuth tris(2-ethylhexanoate) and 3 M of isostearic acid	200	200	200	120
40	Bismuth tris(2-ethylhexanoate) and 3M of oleyl sarcosine	200	200	180	50
45	Bismuth tris(2-ethylhexanoate) and 1½M of octadecyl succinic acid			200	50

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Example 9Screening of Potential Catalysts

5 Other know catalysts for alcohol blocked isocyanates
10 were screened in an acrylic polyol and a MDI polyisocyanate
 blocked with butyl carbitol formulation. The ratio of blocked
 isocyanate to hydroxyl was 1/1.

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	Catalyst Me wt%	MEK double rubs	MEK double rubs
20 Cure temperature, °C		150°C	170°C
No catalyst	0	2	2
Dibutyltin dilaurate	0.18	10	130
25 Bismuth tris(2- ethylhexanoate)	0.18	120	200
Zn bis(2-ethylhexanoate)	0.18	24	200
Al chelate	0.18	20	
30 Zr chelate	0.18	11	
Ti tris(ethyl acetoacetate)	0.18	13	
Zr bis(2-ethylhexanoate)	0.18	10	
35 Mn Naphthenate	0.18	10	
Ca bis(2-ethylhexanoate)	0.18	10	
40 Co bis(2-ethylhexanoate)	0.18	100	
Cr tris(2-ethylhexanoate)	0.18	15	

10 As shown in this screening study only bismuth tris(2-
45 ethylhexanoate), DBTDL and Zn bis(2-ethylhexanoate) showed any
 promise of improved performance.

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Example 10Comparative Example

A bismuth lactate catalyst was prepared according to Feola et. al. (PCT Int. Application WO 9507377). A bismuth dimethylol-propionic salt catalyst was prepared according to Foedde et. al. (Eur. Pat. Appl. EP 690106). A bismuth catalyst was also prepared from an amino acid (glycine) according to Bethoski et. al. (PCT Int. Appl. WO 9810024).

<u>Formulation</u>	<u>Parts by Weight</u>
Epoxy resin of Example 4	251.3
Blocked isocyanate crosslinker of Example 5	118.4
Catalyst	0.25 wt% metal on total resin solids
Lactic acid 85 wt% solution in water	11.5
De-ionized water	618.8
Total Formulation	1000.0

Water-based cationic E-coat formulations were prepared by mixing the epoxy-amine adduct and the blocked isocyanate, with various catalysts respectively into each of the resins blends. Each of the formulations was neutralized with lactic acid to pH 5.0 to 6.0. The resin formulation was then emulsified with water to 30 wt% solids content

The formulations containing the different catalysts were applied after 24 hours on Bonderite 1000 steel panels pretreated with iron phosphate. The cured coatings were evaluated for solvent resistance (methylethylketone double rubs), humidity, corrosion and impact resistance. The results obtained demonstrated the advantage of the catalyst of the

present invention over other bismuth carboxylate catalysts at the same metal concentration. The catalyst of the present invention provides a faster cure rate and better humidity resistance than the comparative catalyst examples. The test results clearly illustrate the superior cure behavior in improved solvent and humidity resistance provided. The catalyst of the present invention provided less blistering at a lower cure temperature than the catalysts of the present art.

Solvent resistance (MEK double rubs)

Catalyst amount: 0.25 wt% metal on total resin solids
Cure time : 20 minutes
Substrate : Bonderite 1000 (pretreated cold rolled steel)
Dry film thickness: 0.85 mil

<u>Cure temp, °C</u>	<u>165</u>	<u>170</u>	<u>175</u>	<u>185</u>	<u>190</u>
No catalyst	5	5	5	20	190
Bismuth tris(isostearate)	80	125	200	200	200
Bi tris(lactate)	75	85	200	200	200
Bi tris(dimethylol-propionate)	50	82	185	200	200
Bi tris(glycinate)	5	22	50	90	200

Humidity resistance Cleveland Condensing Humidity (50°C)

Substrate : Bonderite 1000 panels
Exposure Time : 312 hours
Baking time : 20 minutes
Dry film thickness : 0.85 mil

Catalyst\Cure temp, °C	170		180	
	<u>Gloss 20%</u>	<u>% blister</u>	<u>Gloss 20%</u>	<u>% blister</u>
No catalyst	0.6	100	45.0	45.0

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Bi tris(isostearate)	93.6	25	92.7	0
Bi tris(lactate)	81.0	60	83.1	0
Bi tris(dimethylol- propionate)	52.5	80	89.8	0
Bi tris(glycinate)	2.9	95	54.9	50.0

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Example 11

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A coating formulation was prepared according to the formulation in Example 10.

5 Dry film thickness : 0.6-0.8 mil

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Catalyst amount : 0.25 wt% metal on total resin solids

Substrate : Iron phosphate pretreated steel.

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<u>Catalysts\Cure temp ° C</u>	<u>190</u>	<u>185</u>	<u>180</u>	<u>175</u>	<u>170</u>
No. catalyst	90	20		5	5
DBTDL			63		30
Bi tris(stearate)			200		150
Bi tris(2-ethyl- hexanoate) + 3M Neodecanoic acid			200	120	70
Bi tris(2- ethylhexanoate) + 3M lauric acid			200	185	70

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Claims

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What we claim is:

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1. A method of catalyzing a cationic coating process with a blocked isocyanate as the crosslinking agent wherein the catalyst is selected from the group consisting of a mixture of a salt of bismuth selected from the group consisting of bismuth oxide, bismuth chloride and a carboxylic acid having a hydrocarbon chain of 11 to 36 carbons and a molecular weight in the range of 165-465 and a bismuth carboxylate wherein the carboxylate has a hydrocarbon chain of 11 to 36 carbons and a molecular weight in the range of 165-465.
2. A method according to Claim 1 wherein the salt of bismuth and the carboxylic acid is water insoluble.
3. A method according to Claim 1 wherein the bismuth carboxylate is water insoluble.
4. A method according to Claim 1 wherein the salt of bismuth and a carboxylic acid is a mixture of bismuth and at least two carboxylic acids.
5. A method according to Claim 1, 2, 3, or 4 wherein the carboxylic acid is selected from the group consisting of undecanoic, dodecanoic, palmitic, stearic oleic, isostearic and abietic acids.
6. A method according to Claim 4 wherein the salt of bismuth and a carboxylic acid is a mixture of bismuth tris(2-ethylhexanoate) and a second carboxylic acid, isostearic acid.
7. A method according to Claim 4 wherein the salt of bismuth and a carboxylic acid is a mixture of bismuth tris(2-ethylhexanoate) and a second carboxylic acid, a fatty acid selected from the group consisting of oleyl sarcosine and octadecyl succinic acid.
8. A cationic coating formulation comprising a blend of:
 - a) a cationic resin selected from the group consisting of

- 5 i) an epoxy-amine reaction product: a bisphenol A
type epoxy resin with an epoxy equivalent weight
of between 200 and 2000 and an amine selected
10 from the group consisting of a primary amine, a
5 secondary amine and a tertiary amine;
- 15 ii) an epoxy-polyol reaction product: a bisphenol A
with an epoxy equivalent weight of between 200
and 2000 and type resin and a polyol selected
10 from the group consisting of glycols and glycol
ethers;
- 20 iii) copolymers of cationic monomers selected from the
group consisting of dimethyl-amino-propyl-
methacrylate, dimethyl-amino-ethyl-methacrylate,
dimethyl-amino-propyl-acrylamide and t-butyl-
25 amino-ethyl acrylate with an acyclic or
methacrylic ester monomer optionally with styrene
or acrylonitrile;
- 30 b) a blocked isocyanate crosslinker selected from an
aromatic and an aliphatic isocyanate with a blocking
20 group selected from the group consisting of malonates,
triazoles, ϵ -caprolactam, phenols, ketoxime,
pyrazoles, alcohols, glycols and glycol ethers;
- 35 c) optionally a polyol, a methoxy-polyethylene glycol and
optionally an alcohol, a methoxy-polyethylene-glycol-
25 ether-amine having a molecular weight in the range of
500 to 2000;
- 40 d) 0.01 to 1.0 wt% metal based on the total weight of the
cationic resin blend of a bismuth catalyst selected
from the group consisting of:
- 45 30 i) bismuth carboxylate, a salt of bismuth and a
carboxylic acid having a hydrocarbon chain of 11-
36 carbons, a molecular weight in the range of
165-465;
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ii) a mixture of bismuth oxide with a carboxylic acid having a hydrocarbon chain of 11-36 carbons, a molecular weight in the range of 165-465;

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iii) a mixture of bismuth carboxylates wherein the carboxylic acid has a hydrocarbon chain of 11-36 carbons, a molecular weight in the range of 165-465.

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9. A cationic coating formulation according to Claim 8 the carboxylic acid is selected from the group consisting of undecanoic, dodecanoic, palmitic, stearic oleic, isostearic and abietic acids..

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10. A cationic coating formulation according to Claim 8 wherein the bismuth catalyst is a mixture of bismuth tris(2-ethylhexanoate) and a second carboxylic acid, isostearic acid.

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11. A cationic coating formulation according to Claim 8 wherein the bismuth catalyst is a mixture of bismuth tris(2-ethylhexanoate) and a second carboxylic acid, a fatty acid selected from the group consisting of oleyl sarcosine and octadecyl succinic acid.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/03490

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C08F 20/34; C08G 59/14; C08K 03/20; C08L 33/14, 63/02, 75/12

US CL : 523/415; 524/555; 525/124, 528; 528/49, 55

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 523/415; 524/555; 525/124, 528; 528/49, 55

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST 2.0 (Databases USPT, DWPI, JPAB, EPAB). Search terms: (poly or di)isocyanates or (poly)urethanes, and bismuth carboxylates.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 810245 A1 (ELF ATOCHEM NORTH AMERICA, INC.) 12 MARCH 1997, page 4, LINES 1-4; page 5, lines 13-14, 17, 20 and 24 and page 6, lines 55-56.	1-3, 5, 8 and 9
Y	EP 509437 A1 (KANSAI PAINT CO. LTD.) 21 October 1992, page 2, lines 46-47; page 4, lines 42-43; page 6, lines 54-58 and page 7, Table 1, Sample No. 9.	1-3, 5, 8 and 9
Y	US 5,021,598 A (PATNAIK et al.) 04 June 1991, column 3, lines 7-22, 31-33 and 37-38; and column 8, lines 30-31.	2-6, 9 and 10
Y	JP 04-065417 A (YOKOHAMA RUBBER CO. LTD.) 02 March 1992 (02.03.92), abstracts.	2-7 and 9-11

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
B earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

25 MAY 2000

Date of mailing of the international search report

22 JUN 2000

Name and mailing address of the ISA/US

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/03490

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,584,362 A (LECKART et al.) 22 April 1986, column 1, line 63 to col. 2, line 7 and columns 4-6 table.	2-5 and 9
Y	US 4,786,655 A (GROGLER et al.) 22 November 1988, column 2, lines 4-16 and 41-54.	2, 3, 5 and 9
Y	US 4,868,266 A (MECKEL et al.) 19 September 1989, column 2, lines 7-27 and column 4, line 66.	2, 3, 5 and 9
Y	JP 05-155962 A (YOKOHAMA RUBBER CO. LTD.) 04 December 1991 (04.12.91) abstract.	2, 3, 5 and 9
Y	JP 03-091520 A (YOKOHAMA RUBBER CO. LTD.) 17 April 1991 (17.04.91), abstract.	2, 3, 5 and 9
Y	JP 10-218962 A (NIPPON POLYURETHANE KOGYO KK) 18 August 1998 (18.08.98), abstracts.	2, 3, 5 and 9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/03490

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/03490

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claims 1-7, drawn to a method of catalyzing a cationic coating process with a blocked isocyanate crosslinking agent and a bismuth catalyst.

Group II, claims 8-11, drawn to a cationic coating formulation comprising a cationic resin, a blocked isocyanate crosslinker, an optional polyol and a bismuth catalyst.

The inventions listed as Groups I and II do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: The special technical feature is the combination of a blocked isocyanate crosslinking agent and a bismuth catalyst. European Patent No. 509,437 (KANSAI PAINT) (page 2, lines 46-47 and page 4, line 42) discloses a mixture of a blocked isocyanate and salts of bismuth and organic acids along with a dialkyl tin aromatic carboxylate. The claimed combination does not make a contribution over the prior art, thereby confirming the lack of unity of invention.

This application contains claims directed to more than one species of the generic invention. These species are deemed to lack Unity of Invention because they are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for more than one species to be searched, the appropriate additional search fees must be paid. The species are as follows:

The bismuth catalysts comprising:

- 1) The mixture of bismuth oxide and a C_{11} - C_{24} carboxylic acid within the bismuth catalyst genus of claim 1.
- 2) The mixture of bismuth chloride and a C_{11} - C_{24} carboxylic acid within the bismuth catalyst genus of claim 1.
- 3) The bismuth carboxylate within the bismuth catalyst genus of claim 1.
- 4) The mixture of bismuth and at least two carboxylic acids of claims 4 and 5 from udecanoic, dodecanoic, palmitic, stearic, oleic, isostearic and abietic acids wherein the number and species of carboxylic acids within the mixture are identified.
- 5) The mixture of bismuth tris(2-ethylhexanoate) and isostearic acid of claim 6.
- 6) The mixture of bismuth tris(2-ethylhexanoate) and oleyl sarcosine of claim 7.
- 7) The mixture of bismuth tris(2-ethylhexanoate) and octadecyl succinic acid of claim 7.

The cationic resins of claim 8 comprising:

- i) An epoxy-amine reaction product.
- ii) An epoxy-polyol reaction product.
- iii) Copolymers of cationic monomers wherein the cationic monomers are selected from dimethylamino (propyl or ethyl) methacrylate, dimethylaminopropyl acrylamide or t-butyl-aminoethylacrylate and the comonomers are selected from a (meth)acrylic ester, styrene and/or acrylonitrile.

The claims are deemed to correspond to the species listed above in the following manner:

The bismuth catalysts: claims 1-11.

The cationic resins: claim 8.

Claims 1-11 are generic.

The species listed above do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, the species lack the same or corresponding special technical features for the following reasons: The special technical feature is the combination of a blocked isocyanate crosslinking agent and a bismuth catalyst. European Patent No. 509,437 (KANSAI PAINT) (page 2, lines 46-47 and page 4, line 42) discloses a mixture of a blocked isocyanate and salts of bismuth and organic acids along with a dialkyl tin aromatic carboxylate. The claimed species of bismuth catalysts and cationic resins do not make a contribution over the prior art, thereby confirming the lack of unity of invention.